

## A Study of the Thermistor Method for Molecular Weight Determination

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### Abstract

The temperature of a drop of solution suspended in an atmosphere saturated with the solvent is higher than that of a drop of pure solvent. The resulting difference in temperature, measured by matched thermistors, is proportional to the mole fraction of solute, thus permitting determination of its molecular weight. The apparatus and technique are briefly described and the improvements effected by certain novel modifications to the apparatus and circuitry and variations in the technique are reported. The use of a dynamic flow technique instead of the static drop procedure is described as a means of decreasing some of the variability encountered in placing the sample solution on the thermistor by a hand-manipulated dropper or syringe.

The thermistor method for the determination of molecular weight is one of several that have been classified as thermoelectric methods.<sup>1</sup> In these methods, an indirect electrical measurement is made of the lowering of the vapor pressure of the solvent due to the presence of a solute. As in the cryoscopic and ebullioscopic methods, a related temperature effect is actually measured. In this case, the rise in temperature of a drop of solution suspended in an atmosphere saturated with solvent is measured with a thermistor.

This temperature increase results from the fact that the rate of evaporation is less than the rate of condensation. This difference in rates is proportional to the vapor pressure lowering, which, in turn, is proportional to the mole fraction of solute. If the drop is suspended on a thermistor, the change in temperature that occurs is translated into a resistance change. If a thermistor of high resistance is used to measure this relatively small change in temperature, the

change in resistance becomes essentially proportional to the change in temperature, even though the temperature-resistance curves of thermistors are nonlinear.

The classification as thermoelectric is indicative of this electrical measurement of a temperature change. The thermistor method

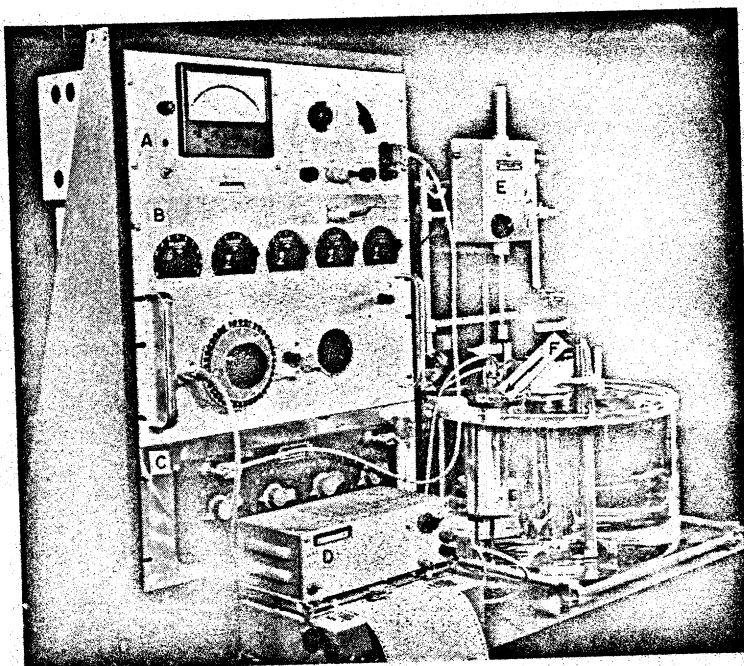


Fig. 1. Molecular weight apparatus. (A) Null detector (microvoltmeter, 1 v. output). (B) Wheatstone bridge circuit. (C) Voltage divider (set to output/input ratio of 0.01). (D) Recorder (10 mv. full scale). (E) Motor-driven buret. (F) Vapor chamber assembly.

designates those procedures in which thermistors, rather than thermopiles or thermocouples, are used as the temperature transducers. At this time, this method provides one of the simplest and most rapid means available for the microdetermination of molecular weight. An apparatus and technique that appeared optimum in these respects were described by Neumayer<sup>2</sup> in 1959. We therefore proceeded to construct a similar apparatus in our laboratory (Fig. 1).

## Apparatus

### Solvent Chamber

The vapor chamber is essentially a copy of Neumayer's design and does not differ from it in any critical details. As in all thermoelectric methods, a reference temperature transducer is included to compensate for vapor chamber temperature fluctuations. The thermistors are of the bead type, sealed in the tips of narrow glass probes. They have a resistance of about 100K at room temperature. The chamber, with the exception of the nylon cap, is immersed in a constant temperature bath which should be regulated to  $\pm 0.01^\circ\text{C}$ . when working with solutions in the 0.01 mole fraction range and to  $\pm 0.001^\circ\text{C}$ . for solutions in the 0.001 mole fraction range.

### Wheatstone Bridge Circuits

The basic Wheatstone bridge circuit is shown in Figure 2. For convenience, and to obtain additional information, a 5-position, 12-pole 4-deck rotary switch was installed. By appropriate wiring, four different Wheatstone bridge circuits are provided which enable one to determine: (1) the change in resistance of the sensing thermistor with respect to the reference thermistor; (2) the resistance of the reference thermistor; (3) the resistance of the sensing thermistor;

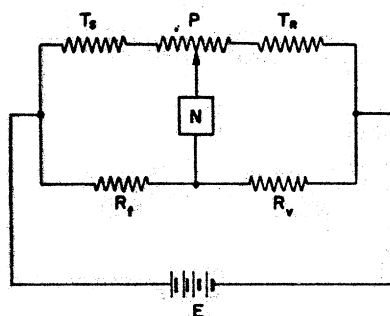


Fig. 2. Wheatstone bridge circuit. ( $T_s$ ) Sensing thermistor (Fenwal type G A51P8, 100 K.); ( $T_r$ ) reference thermistor (Fenwal type GA51P8, 100 K.); ( $P$ ) potentiometer (40 turn, 5000 ohm); ( $N$ ) null detector (microvoltmeter, full scale voltage ranges, 1 v. to 10  $\mu\text{v.}$ ); ( $R_f$ ) fixed resistor (100K, 0.01%); ( $R_v$ ) variable resistance (a series of decade resistors, range 1 ohm to 111,110 ohms); ( $E$ ) 3 mercury cells (Mallory RM-42R).

(4) the value of an unknown external resistance. The fifth position short circuits the input to the null detector for zero adjustment.

From the equation for the Wheatstone bridge circuit in position 1 (shown in Fig. 2), it follows that the change in the variable resistance is proportional to the reciprocal of the change in the sensing thermistor. Again, when using a recorder to plot bridge unbalance, a change in resistance at the sensing thermistor is not linear with respect to change in bridge unbalance. In either case, the nonlinearity is slight because of the relatively small change in resistance in the sensing thermistor.

### **Procedure**

The procedure is briefly as follows:

(1) Rinse both thermistors with solvent by means of an eye dropper through a hole in the plastic cap.

(2) Allow 5 to 10 min. for temperature equilibrium, then balance the bridge by adjusting the potentiometer.

(3) Rinse the sensing thermistor with test solution and follow the response by either balancing the bridge with the variable decade resistance or using a strip-chart recorder to trace the bridge unbalance. The test solution and long eye dropper used to transfer it to the sensing thermistor are kept at the bath temperature.

(4) Record the response 4 min. after placing the test solution on the sensing thermistor. This leads to more reproducible values than does the maximum response which occurs earlier.

### **Critical Factors in Technique**

#### *Rinsing Action*

Our most reproducible results were obtained by the addition of 12 drops at a rate of approximately 1 drop/sec. We were gratified to find that Neumayer<sup>3</sup> had standardized on the same number of drops. A 12-drop rinse is far in excess of the amount necessary to completely replace the solvent on the thermistor. Hence, the need for this amount of rinse must be to satisfy another condition. It can be seen in Figure 3 that in this procedure a very appreciable cooling effect occurs in our assembly. This curve was obtained by feeding the output of the null detector to a strip-chart recorder. Apparently, approximately 12 drops are required to minimize the variability in the cooling effect when this technique is used.

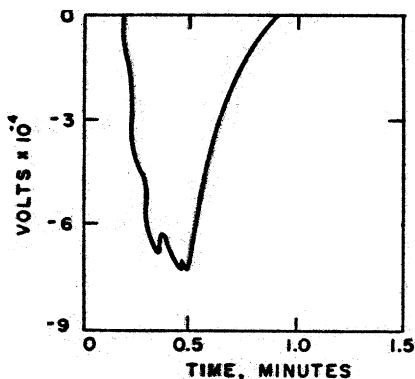


Fig. 3. Bridge unbalance (dropwise technique).

To avoid this cooling effect, we tested a procedure in which the eye dropper containing the solution was kept in the solvent chamber until it reached temperature equilibrium before rinsing. With this technique, a minimum of only 6 to 8 drops of rinse is required. No improvement in reproducibility of response was noted. The response attained with the final drop deposited on the thermistor appears to be a function of the temperature to which the thermistor had risen with the prior drop of rinse. After the first 6 to 8 drops, each additional drop at first tends to cool the thermistor and then to raise it to a slightly higher temperature. Additional drops thus tend to increase the maximum temperature rise but have no detectable effect on the reproducibility. Apparently, the variable cooling effect previously described does not affect the final response any more than the variable heating effect in this technique. This problem of rising thermistor temperature due to condensation was recognized by Tomlinson<sup>4</sup> in his recently published article. It is interesting to note that he standardized on a 10-drop rinse. Here again, a large rinse was used to minimize variability in results.

On the other hand, in a commercial apparatus recently introduced,\* only a 3- to 4-drop rinse is required. The reproducibility of results with this apparatus may depend in part on factors that tend to give a more reproducible rinsing action. Consequently it appears that

\* Model 301 Vapor Pressure Osmometer, Mechrolab, Inc., Mountain View, California. Mention of specific products does not constitute endorsement of those products by the Department of Agriculture over similar products not named.

improvement in the rinsing technique may bring the added benefit of reduced sample size requirement.

#### *Effect of Apparatus Reassembly*

Another critical factor is the necessity for recalibration every time the apparatus is reassembled. We were in the habit of disassembling the apparatus at the close of each day to rinse with new solvent, but did not relate this to our inability to reproduce our calibration value. Neumayer<sup>3</sup> had found that "a variation of 1-2% in the value of  $K$  can be expected due to slight variations in the position of the thermistors with respect to the vapor chamber and the contents of the same."

Reassembly can affect the horizontal displacement of the thermistors and adsorbent lining more than the vertical displacement. Moreover, the distance between a thermistor and the lining is far smaller than the distance from a thermistor to either the top or bottom of the chamber. By taking resistance readings of a single thermistor at various points in the solvent chamber, we found that there was no horizontal temperature gradient. However, the temperature at the top of the chamber was about 0.2°C. less than that at the level of the thermistors. This leads to a continuous process of condensation in the upper portion of the chamber as evidenced by an increase in the level of solvent in the crucible on overnight standing.

Lack of a temperature gradient at the thermistor level indicates no measurable convection in this area despite the vertical temperature gradient. The variation in  $K$  due to reassembly of the chamber probably is caused by variation in the distance between the sensing thermistor and the adsorbent lining, the main source of solvent vapor. We postulate that a vapor pressure gradient is established around the sensing thermistor by the condensation of the solvent on the drop of solution and that the further the thermistor is from the lining the lower will be the response.

#### **Variations in Apparatus and Technique**

##### *Improved Bath Temperature Control*

A problem of excessive temperature cycling occurred in a bath having a knife blade heater with off-on control and an immersion

pump stirrer. This problem was eliminated with a commercial bath having proportional heating control. The solvent chamber undoubtedly was heated more symmetrically in this bath because of the design of the stirrer and heater. The importance of symmetrical heating was discussed by Tomlinson in his study.

#### *Rapid Rinsing Action*

A convenient way in which to rinse a thermistor with approximately the same volume in a relatively reproducible time is to count the number of drops that fall from the thermistor. Ideally, the drop rate should be constant and the same rate applied in each determination. Manually, a significant variation is unavoidable. We therefore sought methods of rinsing that do not depend as much on technique. Our first approach was to design an eye dropper slotted to fit the thermistor and marked at the 0.1 ml. level. Solutions of this volume were then squirted on the thermistor. Results were very erratic, probably due to the fact that air blown on the thermistor removes variable amounts of solution.<sup>3</sup>

#### *Gravity Flow Rinsing*

To test the effect of gravity flow, we used a similar eye dropper having a narrow bore and a stopcock. The eye dropper was filled with 0.1 ml. of solution, the slot fitted to the thermistor, and the fluid released by turning the stopcock. Results were again erratic. Quite probably, the critical factor in this technique was the size of the drop left hanging on the tip of the thermistor, which varied from no drop at all to one just about to fall. Tomlinson has indicated that the effect of drop size is significant; also the procedure for the commercial apparatus specifies a minimum size of drop.

#### *Constant Flow Technique*

The possibility of being required to determine the molecular weight of as little as 1 mg. of sample led to our final approach to the rinsing technique, one that is currently being used. The use of thermistors without the platinum wire winding was tested. It was reasoned that only a few drops of rinse would be necessary in this case if the eye dropper were kept in the solvent vapor chamber until it reached temperature equilibrium before rinsing. Such variables in the rinsing

action as the number of drops, the time between drops and the size of the drop finally deposited were tested.

Difficulty in regulating the size of drops led to a concept of rinsing without drop formation. This was accomplished by sealing a soft glass extension to the end of the glass probe. The response of the modified probe was followed while it was being rinsed with a very slow flow. This flow was obtained by barely venting the eye dropper to the atmosphere by means of a needle valve. Although the flow rate decreased as the head of solution in the eye dropper decreased, a gentle curve rising to an almost steady state resulted. It seemed likely that with a constant slow flow of the proper rate an equilibrium temperature could be reached.

We, therefore, used an American Instrument Company Meniscomatic motor-driven buret to test the effect of various flow rates. With solvent only, a constant temperature was maintained at rates of 0.016 to 0.090 ml./min. At higher rates there was a cooling effect, probably resulting from the fact that the liquid did not have sufficient time to equilibrate to chamber temperature. With a solution of naphthalene in benzene the heating effect increased as the flow rate decreased in the range of 0.110 to 0.045 ml./min.

To test the effect of slower flow rates, we used the plunger of the motor driven buret as a ram to depress the plunger of a  $\frac{1}{4}$  cc. hypodermic syringe. The volume delivered was calculated by multiplying the volume indicated on the buret counter by the ratio of the squares of the diameters of the syringe and buret plungers. The syringe in turn acted as a control to a specially constructed pipet of short length completely inserted in the chamber below the level of the bath. At the first we had difficulties with erratic levels in the entire flow rate range of 0.077 to 0.010 ml./min. These fluctuations were minimized by wrapping the thermistor section of the glass probe with about 10 turns of 28 gage platinum wire. The heating effect increased as the rate decreased in this range, indicating that the optimum rate was probably below 0.010 ml./min. It was not possible with this arrangement to get a reproducible constant flow in this range.

These lower flow rates were finally attained by using a 100  $\mu$ l. syringe in place of the  $\frac{1}{4}$  cc. syringe and pipet. Maximum temperature rise occurred with flow rates in the range of 0.006 to 0.008 ml./min. As can be seen in Figure 4, the temperature rises to a steady



state in about 3 min. The calibration curve for benzil in carbon tetrachloride using steady-state values exhibits a definite curvature rather than a straight line. This is shown in Figure 5. Nonlinear

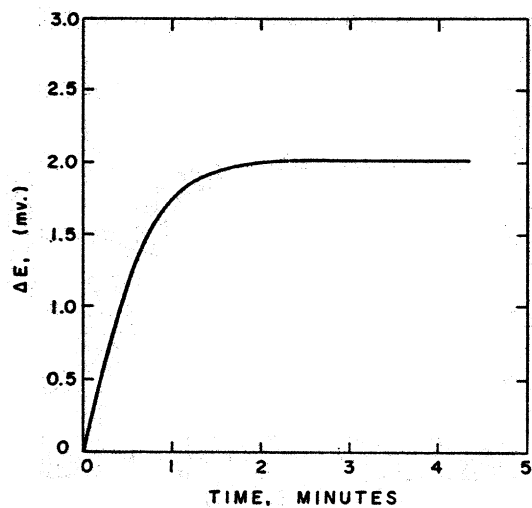


Fig. 4. Bridge unbalance (constant flow).

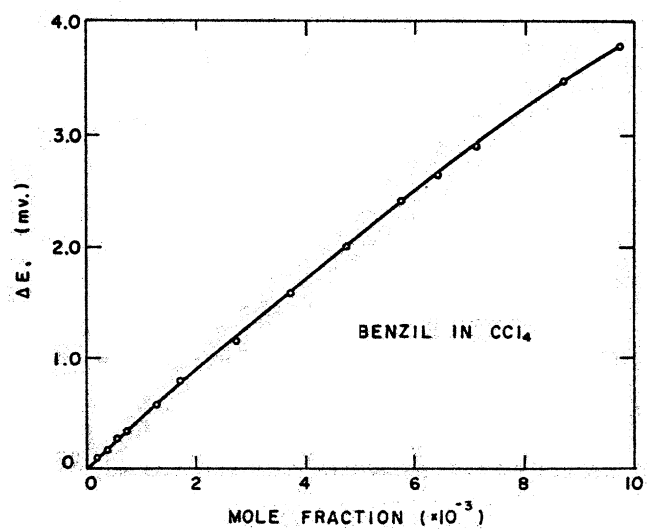


Fig. 5. Calibration curve (constant flow).

calibration with benzil in this solvent has been noted by Tomlinson and with the commercial apparatus.

In an attempt to increase the sensitivity of this method by another order of magnitude we studied the effect of another variable—the distance between the wick and the thermistor bead. In these studies a new cell which was designed to reduce the proportionate area exposed to the atmosphere was used. In the absence of an absorbent lining the response to constant flow was poor and erratic. With an absorbent lining the sensitivity of response increased markedly. We then added a second lining, which reduced the distance between the thermistor and the lining by about one-half. The sensitivity again increased significantly but to a much lesser extent. This indicated that greater sensitivity might be attained by placing absorbent linings in the form of two cylinders around each thermistor. These cylinders were held in place by means of aluminum tubes attached to the metal cap of the solvent chamber. The effect was to put each thermistor in a solvent chamber contained in a single larger solvent chamber.

With constant flow the following results were obtained: (1) variations in flow rate had far less effect on response; (2) lower flow rates (0.003 to 0.004 ml./min.) were suitable; (3) the solvent base line of a single thermistor was quite stable; (4) no significant increase in sensitivity occurred. The increased stability attained with these modifications in apparatus made it possible to use only a single thermistor for determinations in the 0.005 to 0.010 mole fraction range.

In another attempt to increase the sensitivity, the isolating effect of the tubes around the thermistors was eliminated by placing the thermistor beads about 5 mm. inside filter paper tubes of 10 mm. diameter, extending up from the bottom of the cell and held in place by a metal disc containing a hole for each tube. Sensitivity was not increased but good stability was maintained. Variability between successive runs with a 0.01 mole fraction standard solution was less than 1%; with a 0.001 mole fraction solution, about 2%; and with a 0.0001 mole fraction solution, about 10%. This indicates that at least rough estimates of molecular weight can be made on very dilute solutions, a point of importance when working with high molecular weight material of low solubility. The limiting factor appears to be the stability of our thermistor-bridge circuit because the stability of the base line and the response to solution flow were both  $\pm 0.5$  ohm.

### Calculations

Figure 6 shows a plot of resistance change ( $\Delta R$ ) versus mole fraction of azobenzene in chloroform by the dropwise technique. With this method the experimental error was as great as or greater than any nonlinearity in the plot so the molecular weight was calculated by the following equation:

$$M.W._{solute} = (g. \text{ solute} \times M.W._{solvent}/g. \text{ solvent})[(K/\Delta R) - 1]$$

where  $K$  is the ratio of  $\Delta R$  to mole fraction for a standard sample. The nonlinearity of the calibration curve for the constant flow technique using benzil in carbon tetrachloride, Figure 4, was greater than

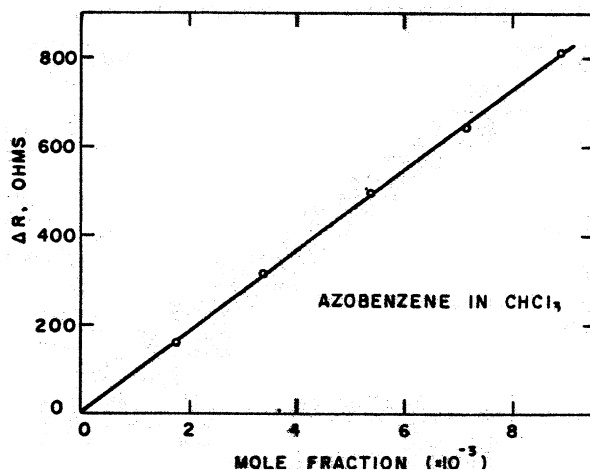


Fig. 6. Calibration curve (dropwise technique).

the experimental error. It was therefore necessary to determine the mole fraction of an unknown sample from the curve and calculate the molecular weight by:

$$M.W._{solute} = (g. \text{ solute} \times M.W._{solvent}/g. \text{ solvent})[(1/MF) - 1]$$

where MF is the mole fraction value interpolated from the standard curves.

## Conclusions

This study has demonstrated the feasibility of a constant flow technique in the thermistor method for the determination of molecular weight. This procedure eliminates much of the variability caused by manually placing the sample solution on the thermistor. The response is determined when the system is at a steady state rather than at a maximum or some slowly changing state past the maximum. Transient effects are readily identified and eliminated. The net effect is to permit reasonably accurate determinations with solutions as dilute as 0.001 mole fraction and approximations with solution in the 0.001 to 0.0001 mole fraction range. Finally, constant flow affords the possibility that with proper instrumentation a new parameter can be available for continuous measurement in such areas as process control and kinetic studies.

## References

1. Bonnar, R. V., M. Dimbat, and F. H. Stross, *Number-Average Molecular Weights*, Interscience, New York-London, 1958.
2. Neumayer, J. J., *Anal. Chim. Acta*, **20**, 519 (1959).
3. Neumayer, J. J., private communication, 9/26/60.
4. Tomlinson, C., *Mikrochim. Acta*, **1961**, 457.

## Discussion

**S. Z. Lewin** (*New York University, New York*): I would like to suggest that a direction in which the sensitivity and stability of the thermoelectric method may be improved *electronically* appears to have been relatively unexplored or unexploited. Most investigators currently use d.c. bridges; however, in this type of circuit, the final read-out signal includes, along with the desired bridge unbalance signal, the entire broad spectrum of noise signals from thermal noise in the thermistors, tube noise in the amplifier, etc. If an a.c. bridge is used, and a sharply-tuned amplifier is utilized, then it is possible to reject the noise, and selectively read out the desired bridge signal. With adequate attention to grounding and shielding of the bridge, the sensitivity of signal detection should be at least an order of magnitude greater than is possible with a d.c. bridge.

**C. L. Hilton** (*U.S. Rubber Co., Wayne*): You mentioned chloroform as one of your solvents. Did you remove the ethanol used for stabilization of the chloroform? We have not obtained good results with reagent grade chloroform.

**C. L. Ogg**: We have used spectral grade solvents in our work but others have reported satisfactory results using less pure solvents providing the chamber is charged with the same solvent used to dissolve the sample and reference material.

**H. A. Sachse** (*Keystone Carbon Co., St. Marys*): How about self-heating of the thermistor?

**C. L. Ogg**: The self-heating of the thermistors can be avoided by limiting the voltage in the thermistor between 0.5 and 20  $\mu$ v. depending on the size of the thermistor and the medium in which it operates.

**R. N. Rogers** (*University of California, Los Alamos*): Have you tried Zehner diode power supplies to replace mercury cells?

**C. L. Ogg**: We have used only the mercury cells.

**S. Eriksen** (*University of Wisconsin, Madison*): How much current do you use through your bridge? (One must consider self-heating.)

**C. L. Ogg**: We have not determined this but it can be calculated. We use three mercury cells as our voltage source and 100K thermistors.

**S. Eriksen**: Sensitive Research Instruments of Canada sells a light beam galvanometer amplifier for d.c. signals which is capable of the amplifications required but without associated a.c. amplifier noise.

**C. L. Ogg**: Amplifier noise and variability in contact potentials are two of the factors which limit the sensitivity of our apparatus. These can be reduced and the stability and sensitivity increased.